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Changes of spin dynamics in multiferroic $Tb_{1-x}Ca_xMnO_3$

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ABSTRACT

We report the results of a series of μSR measurements performed on polycrystalline and single crystalline $Tb_{1-x}Ca_xMnO_3$, with $x = 0$, 0.05 and 0.1. Analysis of the data indicates that the Néel transition temperature around 40 K for the undoped sample is in agreement with the previous result obtained by susceptibility measurement. We further find a peculiar behavior related to the relaxor ferroelectric of magnetic origin for 5% Ca doping. This type of relaxor is suggested to be governed by spin fluctuations due to inhomogeneity in the spiral magnetic ordering induced by the A-site Ca doping. It is shown that the 5% Ca doping appears to induce faster reduction of spin fluctuation with decreasing temperature. Our μSR data in applied longitudinal fields (LF) also indicate the possible occurrence of inhomogeneous internal field although a more detailed study is required for its clarification and verification.

1. Introduction

The magnetic origin of the ferroelectrics has attracted much attention due to the wide-ranging potential new applications of these functional materials. These type of materials have been reported to exhibit a common transformation from collinear spin ordering to spiral spin ordering. The associated spontaneous polarization invariably appears in the direction perpendicular to the spiral propagation vector and spin rotation axis [1–3]. Among the most intensively investigated materials in this class is $TbMnO_3$ because of its relatively simple magnetic structure, and the remarkable polarization flop occurring in the presence of magnetic field. The different wave vectors of the spiral magnetic structures and hence the associated polarizations observed in different $RMnO_3$ compounds have stimulated further investigations to explore the ferroelectricity in these perovskites as a function of the lattice and charge degrees of freedom. The results showed a large magnetocapacitance for $DyMnO_3$ [4], while only an electric polarization was found in applied magnetic field for $GdMnO_3$ [5]. These different effects are known to be related to different A-site ions in the perovskite structure which are responsible for the spiral magnetic ordering. A systematic study of A-site rare-earth doping has been reported in $(Eu,Y)MnO_3$ [6]. However, the effects of A-site alkali-earth doping remain largely unexplored.

Recently, a systematic investigation of A-site doping with Ca in $TbMnO_3$ has shown that a small amount of Ca dopant might reduce the long range spiral ordering and result in a relaxor behavior. Further increment of Ca doping was found to result in a spin glass state and the disappearance of electric polarization [7]. Complementing those findings, we report in this paper the result of a study on spin dynamics of Ca-doped $TbMnO_3$ based on muon-spin relaxation measurement.

2. Experimental

The measurements of ZF-μSR and LF-μSR with applied magnetic field up to 3950 Oe were performed at various temperatures in the RIKEN-RAL Muon Facility at the Rutherford-Appleton Laboratory in the UK, using a pulsed positive muon beam. The asymmetry parameter $A(t)$ at a time t is defined as $A(t) = [F(t) - \alpha B(t)]/[F(t) + \alpha B(t)]$, where $F(t)$ and $B(t)$ are the total muon events counted by the forward and backward counters, respectively, while α is the calibration factor reflecting the relative counting efficiencies between forward and backward counters. Both polycrystalline as well as the single-crystalline samples of $Tb_{1-x}Ca_xMnO_3$ with $x = 0$, 0.05 and 0.1 were used in this experiment. Detailed preparation processes and structural as well as physical characterizations of the samples were reported in Ref. [7].

3. Discussions

Fig. 1 shows the μSR time spectra for polycrystalline $TbMnO_3$ obtained at various temperatures. The muon-spin polarizations were clearly observable from 70 to 40 K, which delay rapidly indicating that the system has entered the paramagnetic state.

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Nevertheless, the fact that they all vanish in the very short period of 1 μs can be attributed to the influence of strong internal field fluctuations at the muon site arising from the Tb and Mn moments. Meanwhile the initial asymmetry at $t = 0$ decreases with decreasing temperature and the time spectrum becomes virtually flat below 35 K, all the way down to 5 K, implying the occurrence of the magnetic ordered state below 35 K.

The time spectra were analyzed using the exponential function $A(t) = A_0 \exp(-\lambda t)$, where A_0 is the initial asymmetry at $t = 0$ and λ is the depolarization rate of the muon spin. It should be noted that the depolarization process in this case took place within a time shorter than the muon pulse width to allow a meaningful analysis of two or multi-component contributions. The solid lines in Fig. 1 show the best-fit to the data. The resulted A_0 and λ variations against the temperature are plotted in Fig. 2. The A_0 is seen to decrease monotonously with decreasing temperature and reaching its near zero value below 35 K. On the other hand, the λ increases with decreasing temperature, and reaches its maximum at about 40 K, before declining sharply to nearly zero below 35 K. Both the monotonic decrease in A_0 and the appearance of a peak of λ in their temperature dependencies are typical for a magnetic system going into the magnetic ordered state. Thus, the magnetic transition temperature is estimated to lie between 35 and 40 K from the current μSR study. This estimated value is in good agreement with the Néel temperature, T_N, obtained from a previous magnetic measurement [5]. Unfortunately, the related spin dynamics taking place within the narrow transition temperature region around 40 K could not be investigated or verified in this experiment, due to the limited pulse width of the muon beam at the RIKEN-RAL muon facility, which has a minimum half width of about 70 ns. Further, it is worth pointing out that in view of the disappearance of the muon-spin relaxation below 35 K, the possible occurrence of spiral magnetic ordering at 27 K could not be investigated as well.

Recently, we found an interesting effect in the Ca-doped $TbMnO_3$ single crystal revealed by typical response of relaxor ferroelectric at 5% Ca doping level characterized by the appearance of a broad peak in the dielectric response at the temperature where a sharp peak was observed in the undoped crystal [7]. The diffraction peak at the incommensurate wave vector observed by neutron diffraction measurement on a single-crystalline sample as reported in the same reference [7] also showed that it becomes weaker and broader compared to undoped case. This was suspected to be related to the relaxor behavior as the ferroelectric properties of this material is known to have a magnetic origin. The observed peak broadening and weakening phenomenon was further suggested to be associated with a decreased coherence length of the Mn-spin spiral structure caused by the weakening of the next-nearest neighbor superexchange interactions [8]. However, this suggested weakening decoupling has yet to be observed directly.

In order to investigate the above-mentioned effect of Ca doping on the magnetic ordered state, a ZF-μSR measurement has been carried out at various temperatures using the single crystalline sample of 5% Ca doping. Fig. 3 shows the resulted time spectra of ZF-μSR. At high temperatures around 100 K, a fast depolarization behavior was observed. With decreasing temperature, the asymmetry component of the fast depolarization process decreases and vanishes below about 50 K. This is similar to the disappearance of the fast depolarization process due to strongly fluctuating Tb and/or Mn moments as observed in the case of $x = 0$. In other words, the muon-spin asymmetry was also lost within the time resolution of the pulsed muon beam in this case. We recall however that in the case of $x = 0$, fast depolarization behavior remains observable even at 40 K, while it is already completely lost at 50 K in the case of $x = 0.05$. This means that as a result of 5% Ca doping, the spin fluctuations of Tb and/or Mn moments in the $x = 0.05$ sample were slowed down with decreasing temperature at a considerably faster rate as compared to the undoped case. This has led us to suggest that the fluctuations of Tb and/or Mn spins were weaker in the ground state of $x = 0.05$ sample than the spin fluctuations in the undoped sample.

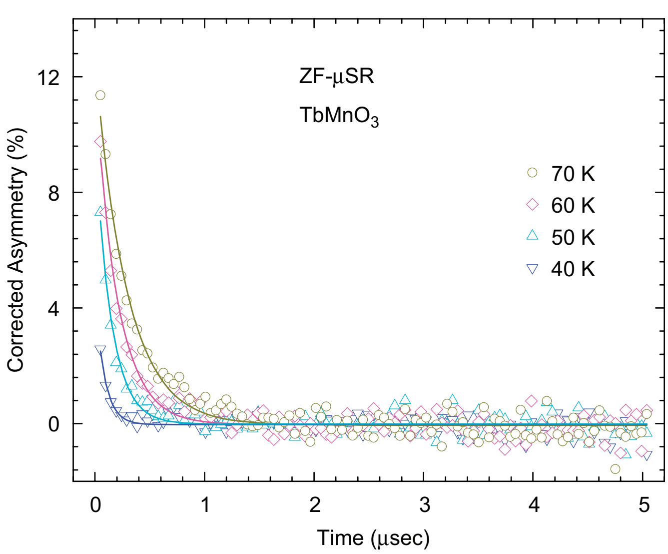

Fig. 1. The temperature dependence of ZF-μSR spectra of $TbMnO_3$. The solid lines are the best fits using exponential function described in the text. No asymmetry was detected at $T \leqslant 35$ K.

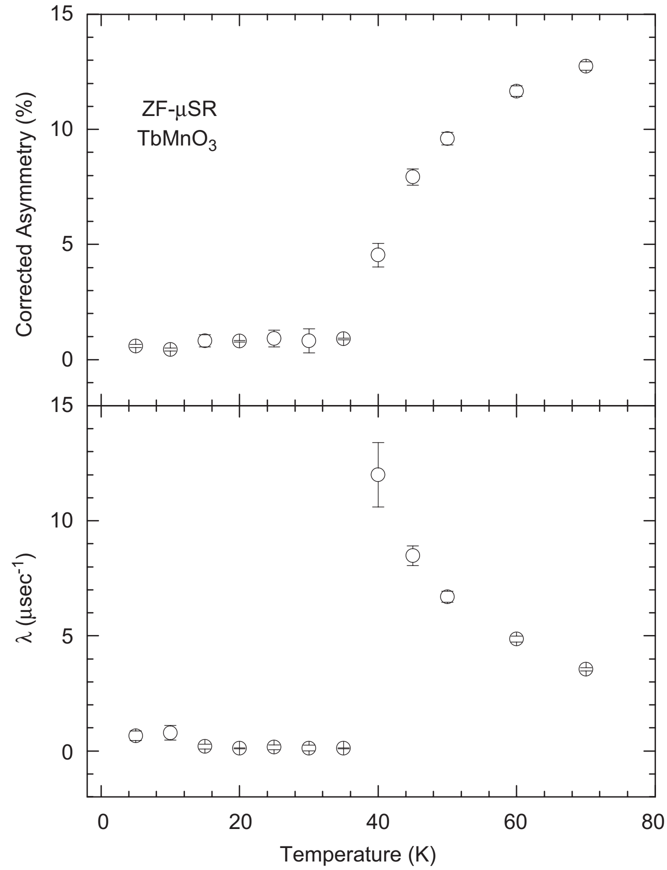

Fig. 2. (a) The temperature dependence of the corrected asymmetry of zero-field fast muon relaxation spin in $TbMnO_3$ and (b) the temperature dependence of zero-field muon-spin relaxation rate in $TbMnO_3$.

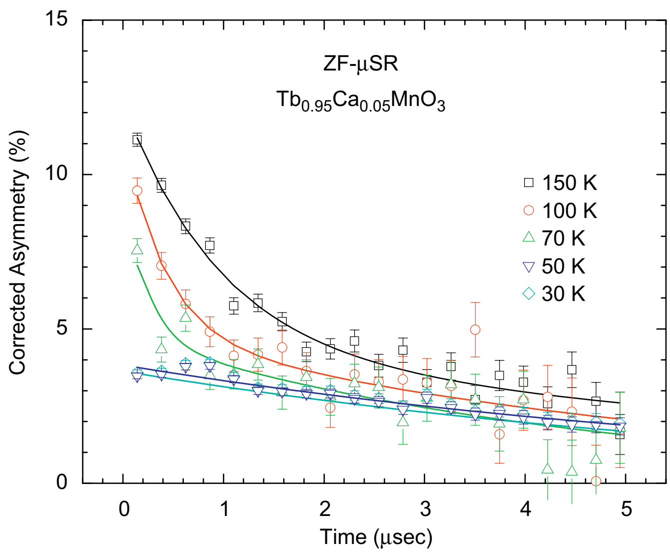

Fig. 3. The temperature dependence of the corrected asymmetry of zero-field fast muon relaxation spin in $TbCa_{0.05}MnO_3$.

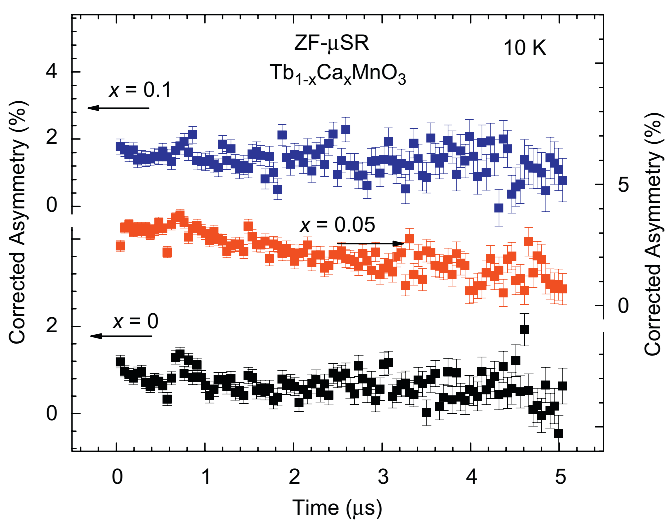

Fig. 4. The ZF-μSR spectra of $Tb_{1-x}Ca_xMnO_3$ with $x = 0$, 0.05 and 0.1 at 10 K.

The above-mentioned effect of Ca doping on the magnetically ordered state was further investigated by a ZF-μSR measurement carried out at 10 K using the same single crystalline sample. Fig. 4 shows the comparison between the effects of different Ca doping concentrations at that temperature. It is observed that the asymmetry of the 5% Ca-doped single crystal sample appears to exhibit some relaxation process in contrast to the relatively flat behaviors shown by the undoped and the 10% Ca-doped samples.

For the purpose of obtaining more information about the internal field at the muon site, the μSR measurement in various applied longitudinal fields was repeated at the same temperature. The result is presented in Fig.5. At this temperature, the sample clearly shows a magnetic ordered state. The time spectrum is practically flat at each LF while the asymmetry seems to recover with increasing LF although the fast depolarization behavior observed at temperatures about 50 K and higher was not recovered even at the applied maximum LF of 4 kG. In order to ascertain the extent of the recovered asymmetries, the instrumental shift of the base line of the time spectrum, which marks the zero level of the asymmetry, was calibrated in each LF. Based

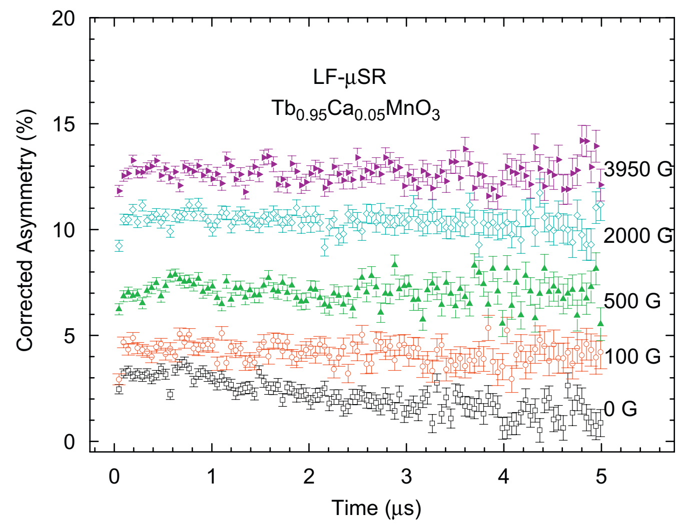

Fig. 5. The LF-μSR spectra at 10 K for 5% Ca doped $TbMnO_3$.

on the result of this calibration measurement, it was found that the asymmetry lost in the time spectrum of Fig. 4 was only partially recovered by LF, indicating that the fluctuating internal fields coming from magnetically ordered Tb and/or Mn spins remained quite large such that the muons cannot be decoupled from these internal fields even by the applied maximum field of 4 kG.

We note that in this study, no sign of coherent muon-spin precession has been observed at all measured temperatures in the magnetic ordered state. This is likely the consequence of the limited time resolution of the pulsed muon beam, and it points to the need to perform additional investigations using the dc muon beam with higher time resolution. In spite of that, we may suggest from our current data the possible appearance of inhomogeneous internal field at the muon site due to the 5% Ca doping on the $TbMnO_3$ compound. This suggestion is consistent with the inhomogeneous nature of the spin alignment revealed by the neutron scattering measurement [7].

4. Conclusion

We have obtained the Néel transition temperature of around 35 K for the polycrystalline $TbMnO_3$ sample is in good agreement with the previous result obtained by magnetic susceptibility measurement. We have further shown in this experiment that the spin fluctuation associated with the inhomogeneous spiral magnetic ordering induced by the A-site doping had a remarkable effect on the properties of relaxor ferroelectric. Specifically the 5% Ca doping appears to induce more effective reduction of spin fluctuation by lowering the sample temperature. The possible occurrence of inhomogeneous internal field was also suggested by μSR data obtained in applied LF, although an additional measurement at higher resolution is needed for its verification.

Acknowledgments

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